

DESCRIPTION

ELECTRON SPECTROSCOPY ANALYSIS METHOD AND ANALYTICAL APPARATUS

Technical Field

[0001] The present invention relates to an electron spectroscopy analysis method and analytical apparatus for executing a desired analysis with respect to a surface or a depth direction of a sample to be analyzed by irradiating a high-energy particle to the sample to be analyzed under a vacuum atmosphere and detecting a number and a kinetic energy of electrons emitted from the sample to be analyzed on the basis of a photoelectric effect.

Background Art

[0002] The electron spectroscopy analytical apparatus is widely used in a correlation analysis of functional physical property, a quality control, a process analysis work and the like for improving a product performance, for example, with respect to various samples prepared in a developing process and a manufacturing step of the various samples. In particular, an X-ray photoelectron spectroscopy analytical apparatus employing a characteristic X-ray as the high-energy particle is widely used for analyzing contamination, a composition ratio of a composition material and the like at a depth of approximately 5 nm of a surface layer of a sample.

[0003] Furthermore, an ultraviolet ray photoelectron spectroscopy analytical apparatus employing an ultraviolet ray as the high-energy particle is widely used for analyzing a work function change, a chemical state of a composition

material and the like at a depth of approximately 5 nm of a surface layer of a sample. Incidentally, an electron, a gamma ray, a synchrotron orbital radiation, a laser beam, an ion, a positron or the like may be used as the high-energy particle 5 source, in addition thereto.

[0004] A photoelectron spectroscopy analysis method is an analysis method for analyzing an element within a sample by irradiating a high-energy light to a surface of a sample, and measuring a number and a kinetic energy of electrons emitted 10 on the basis of a photoelectric effect. Since not only the photoelectric spectroscopy analysis method is capable of measuring an elemental composition on a surface of a sample but also the method is excellent in an analysis of a chemical state of a material, the photoelectric spectroscopy analysis 15 method is utilized for an analysis of an oxidation state of an organic thin film sample, an oxidation state of silicon on a surface of a semiconductor device or the like. At this time, since the surface of the sample is unavoidably covered by a contaminant, such as oil, fat, water or the like, a 20 preliminary washing treatment, which removes the contaminant generally by means of a sputtering ion source, is executed in many cases.

[0005] In the meanwhile, in a preliminary cleaning treatment of irradiating a rare gas ion (for example, an Ar 25 ion) to a surface of a sample, which is widely used in a conventional photoelectron spectroscopy analytical apparatus, a surface damage is caused at the time of ion-etching the

surface of the sample. Accordingly, a range, to which the preliminary cleaning treatment of irradiating the rare gas ion to the surface of the sample is applied, has been conventionally limited to an analysis of a metal or a 5 semiconductor having a small surface damage, or an analysis of a very limited oxide.

[0006] Accordingly, in recent years, there have been proposed various methods as an etching method for a surface of a sample (see, for example, to patent document 1, non-patent 10 document 2, patent document 3 and non-patent document 4).

[0007] In the patent document 1 mentioned above, there is disclosed an analysis method for preparing a sample showing information in a depth direction by cutting the sample by a known tool, such as a diamond cutter or the like.

15 [0008] In the non-patent document 2 mentioned above, it is described that a method for exposing an interior portion of a sample to a surface by cleavage or scribing of the sample and analyzing the interior portion of the sample by a surface analysis method is widely known.

20 [0009] In the patent document 3 mentioned above, it is disclosed that a contaminant having a small damage is removed by an etching of a surface of a sample using a cluster ion comprised of one hundred or more atomic atoms or molecules.

[0010] In the non-patent document 4 mentioned above, it is 25 mentioned that a surface of a sample is cleaned by dashing dry ice small particles to a surface of a sample.

Patent Document 1

Japanese Unexamined Patent Publication No. 2002-365183

Non-patent Document 2

ASTM E1078-97 of American National Standard International Standard, Article 11, 3, 4, 1996

5 Patent Document 3

Japanese Unexamined Patent Publication No. H08-122283

Non-patent Document 4

J. Vac. Sci. Technol., B9, p. 1970, 1991

Disclosure of Invention

10 Problem to Be Solved by the Invention

[0011] At the time of using the methods of the patent document 1 and the non-patent document 2 mentioned above, as described in American National Standard International Standard (ASTM E1078-97, Article 11, 3, 4, 1996), it is necessary to uniformly etch at a range which is larger than a diameter of an analysis probe of an electron beam, an X-ray or the like and which corresponds to a magnitude of the analysis probe. Furthermore, particles, such as cut scraps or the like are frequently left on the surface of the sample, and it is preferred to make an analysis while avoiding them. Accordingly, in an analysis method which can employ a small probe, such as an Auger electron spectroscopy analysis, these analysis methods are generally used, however, these analysis methods are not suitable for an analysis method employing a comparatively large probe, such as a photoelectron spectroscopy analysis.

[0012] In the method of the patent document 3 mentioned

above, since it is necessary to prepare a cluster by preparing high-pressure gas and utilizing a gas jet generated by a pressure difference from a vacuum chamber, a large-scale equipment is necessary for being used for a surface analysis 5 requiring an ultra-high vacuum apparatus, and a cost is increased. Furthermore, since speeds of one hundred or more clusters are different depending on the number of the clusters, a surface irregularity tends to be caused, for example, in a scanned range, and it is difficult to execute a uniform 10 etching.

[0013] In the non-patent document 4 mentioned above, since a neutral particle is employed in place of an ion, a repeatability does not exist in an operation, and it is difficult to quantitatively estimate an etching amount. 15 Furthermore, in order to apply the non-patent document 4 to an analysis of a surface of a sample, it is necessary to execute the analysis by an analytical apparatus under an ultra-high vacuum. Therefore, the large-scale equipment is required in the same manner as in the case of the cluster ion mentioned 20 above, and the cost is also increased.

[0014] Accordingly, an object of the present invention is to provide an electron spectroscopy analysis method and analytical apparatus which can uniformly etch a surface of a sample with an improved repeatability, and can etch at a low 25 cost without requiring any large-scale equipment.

Means for Solving the Problem

[0015] In order to achieve the above-mentioned object, in

accordance with a first aspect of the present invention, there is provided an electron spectroscopy analysis method for executing a desired analysis with respect to a surface of a sample to be analyzed by irradiating a high-energy particle to 5 the sample to be analyzed under a vacuum atmosphere, and detecting a number and a kinetic energy of electrons emitted from the sample to be analyzed on the basis of a photoelectric effect, wherein the method includes steps of ionizing a fullerene, irradiating the fullerene ionized to the surface of 10 the sample to be analyzed before irradiating the high-energy particle to the sample to be analyzed, and removing a contaminant present on the surface of the sample to be analyzed.

[0016] Furthermore, in accordance with a second aspect of 15 the present invention, there is provided an electron spectroscopy analysis method for executing a desired analysis with respect to a depth direction of a sample to be analyzed by irradiating a high-energy particle to the sample to be analyzed under a vacuum atmosphere, and detecting a number and 20 a kinetic energy of electrons emitted from the sample to be analyzed on the basis of a photoelectric effect, wherein the method includes steps of ionizing a fullerene, irradiating the fullerene ionized to the surface of the sample to be analyzed before irradiating the high-energy particle to the sample to 25 be analyzed, and ion-etching the surface of the sample to be analyzed.

[0017] Furthermore, in accordance with a sixth aspect of

the present invention, there is provided an electron spectroscopy analytical apparatus for executing a desired analysis with respect to a surface of a sample to be analyzed by irradiating a high-energy particle to the sample to be
5 analyzed from a high-energy particle irradiating unit under a vacuum atmosphere, and detecting a number and a kinetic energy of electrons emitted from the sample to be analyzed by an analyzer on the basis of a photoelectric effect, wherein the apparatus includes an ion gun for ionizing a fullerene and
10 irradiating the fullerene ionized, and the apparatus ionizes the fullerene, and irradiates the fullerene ionized from the ion gun to the surface of the sample to be analyzed before irradiating the high-energy particle to the sample to be analyzed, thereby removing a contaminant present on the
15 surface of the sample to be analyzed.

[0018] Furthermore, in accordance with a seventh aspect of the present invention, there is provided an electron spectroscopy analytical apparatus for executing a desired analysis with respect to a depth direction of a sample to be
20 analyzed by irradiating a high-energy particle to the sample to be analyzed from a high-energy particle irradiating unit under a vacuum atmosphere, and detecting a number and a kinetic energy of electrons emitted from the sample to be analyzed by an analyzer on the basis of a photoelectric effect,
25 wherein the apparatus includes an ion gun for ionizing a fullerene and irradiating the fullerene ionized, and the apparatus ionizes the fullerene and irradiates the fullerene

ionized from the ion gun to the surface of the sample to be analyzed before irradiating the high-energy particle to the sample to be analyzed, and ion-etches the surface of the sample to be analyzed.

5 Effect of the Invention

[0019] In accordance with the present invention, it is possible to uniformly apply an etching process to a surface of a sample to be analyzed to such a level that a damage on the surface of the sample to be analyzed is negligible even when a 10 contaminant on the surface of the sample to be analyzed is removed, by irradiating a fullerene ion beam to the surface of the sample to be analyzed before irradiating a high-energy particle to the surface of the sample to be analyzed. Accordingly, it is possible to precisely analyze a composition, 15 a chemical state and the like of the sample to be analyzed.

[0020] Furthermore, since an ion gun irradiating a fullerene ion beam is not large, as compared with an apparatus forming a cluster (an ion source), a large-scale equipment is not required, and it is possible to restrict a cost increase.

20 Best Mode for Carrying Out the Invention

[0021] A description will be given below of illustrated embodiments in accordance with the present invention.

<Embodiment 1>

Fig. 1 is a skeleton schematic view showing an electron 25 spectroscopy analytical apparatus in accordance with an embodiment 1 of the present invention. An electron spectroscopy analytical apparatus 1 in accordance with the

present embodiment is provided with a vacuum chamber 2 to which a vacuum pump system (not shown) is connected, as shown in Fig. 1. And a sample stage 5 for arranging and fixing a sample (an analyzed object) 4 to be carried from an external 5 portion by the carrier device 3 is provided within the vacuum chamber 2.

[0022] Furthermore, in an upper portion of the vacuum chamber 2, there are placed a high-energy particle irradiating unit 6 irradiating a high-energy particle (an X-ray in the 10 present embodiment) to the sample 4 mounted on the sample stage 5, an electron energy analyzer 7 for analyzing an energy of electrons emitted from the surface of the sample 4 by the high-energy particle irradiated to the surface of the sample 4 from the high-energy particle irradiating unit 6, and an ion 15 gun 8 irradiating a C60 ion beam (carbon 60 cluster ion beam) to the surface of the sample 4. As the ion gun 8 irradiating the C60 ion beam, a known ion gun can be employed. In the present embodiment, as the high-energy particle irradiating unit 6, a dual characteristic X-ray source provided with a 20 target of aluminum and copper is used.

[0023] Next, a description will be given of an electron spectroscopy analysis method by the electron spectroscopy analytical apparatus 1 in accordance with the embodiment 1 of the present invention mentioned above. In the present 25 embodiment, a polytetrafluoroethylene (PTFE) $((CF_2)_n)$ is employed as the sample 4, and an X-ray photoelectron spectroscopy analysis of the polytetrafluoroethylene (PTFE)

$((CF_2)_n)$ as the sample 4 is executed.

[0024] First, the sample 4 is mounted on the sample stage 5 within the vacuum chamber 2 regulated to a predetermined pressure through an open gate valve 9 by driving a carrier arm 5 3a within the carrier device 3 which is regulated to a predetermined pressure (a degree of vacuum) by evacuating using a vacuum pump system (not shown). The pressure within the vacuum chamber 2 is not particularly limited, however, in view of preventing contamination or the like on the surface of 10 the sample 4, it is preferred to set the pressure to 1×10^{-5} Pa or less. In the present embodiment, the pressure within the vacuum chamber 2 is set to 5×10^{-7} Pa.

[0025] Furthermore, the ion gun 8 is actuated and the C60 ion beam is irradiated to the surface of the sample 15 (polytetrafluoroethylene (PTFE) $((CF_2)_n)$) 4. On the basis of the collision of the C60 ion beam with the surface of the sample 4, a contaminant, such as water, oil, fat, an inorganic material or the like and an oxide film attached to the surface of the sample 4 are uniformly etched so as to be removed. The 20 irradiation conditions of the C60 ion beam in the present embodiment at this time are set such that the accelerating voltage is 2 kV, the ion current is 10 nA, the irradiating time is 60 sec, and the scanning range on the surface of the sample 4 is 5 mm \times 5 mm.

25 [0026] Thereafter, a composition, a chemical state change and the like on the surface or in the depth direction of the sample 4 are analyzed (by an X-ray photoelectron spectroscopy

analysis) by the electron energy analyzer 7, on the basis of the electrons emitted from the sample 4 by actuating the high-energy particle irradiating unit (the dual characteristic X-ray source) 6 and irradiating the characteristic X-ray to the 5 surface of the sample 4. The irradiated characteristic X-ray in the present embodiment at this time has an energy of 1.4867 keV, and aluminum is employed as a target of the characteristic X-ray.

[0027] For the electron spectroscopy analysis by means of the X-ray beam mentioned above, it is necessary to restrict a damage on the surface of the sample 4 caused by the C₆₀ ion beam irradiated from the ion gun 8 to the minimum. Taking the above-mentioned points into consideration, in order to securely acquire an X-ray photoelectron spectroscopy spectrum 15 as mentioned below, the accelerating voltage of the C₆₀ ion beam is preferably 30 kV or less, and more preferably 10 kV or less and 300 V or more.

[0028] As mentioned above, in accordance with the embodiment 1 of the present invention, the uniform etching 20 process is executed by irradiating the C₆₀ ion beam to the surface of the sample (polytetrafluoroethylene (PTFE) ((CF₂)_n)) 4 from the ion gun 8 before irradiating the characteristic X-ray to the surface of the sample 4 from the high-energy particle irradiating unit (the dual characteristic X-ray source) 6, whereby a contaminant, such as water, oil, fat, an inorganic material or the like and an oxide film attached to 25 the surface of the sample 4 are removed. In order to evaluate

the effect of the etching process on the surface of the sample
4 on the basis of the irradiation of the C₆₀ ion beam, the
quantitative value of the surface of the sample 4 is measured.
As a result, carbon is approximately 35 %, fluorine is
5 approximately 65 %, and other elements are hardly detected.

[0029] The results of the quantitative value are
sufficient to estimate that the chemical composition of the
sample 4 is constituted by the polytetrafluoroethylene (PTFE)
((CF₂)_n), and as a result of observing the surface of the
10 sample 4 by an electron microscope, the damage on the surface
of the sample 4 is small enough to be negligible.

[0030] In the meanwhile, the quantitative value on the
surface of the sample 4 in the case wherein the C₆₀ ion beam
is not irradiated to the surface of the sample
15 (polytetrafluoroethylene (PTFE) ((CF₂)_n)) 4 is measured. As a
result, carbon is approximately 46 %, fluorine is
approximately 49 %, oxygen is approximately 3 %, and sodium is
approximately 2 %. As mentioned above, since the surface of
the sample 4 is contaminated in the atmospheric air, not only
20 the elements which are not contained in the sample 4 are
detected, but also a quantitative value which is far from the
quantitative value in the inner portion of the sample 4 is
obtained.

[0031] Furthermore, in the embodiment 1 in accordance with
25 the present invention mentioned above, the C₆₀ ion beam is
irradiated to the surface of the sample
(polytetrafluoroethylene (PTFE) ((CF₂)_n)) 4, however, the

quantitative value on the surface of the sample 4 in the case wherein an Ar ion is irradiated to the sample (polytetrafluoroethylene (PTFE) ((CF₂)_n)) 4 is measured for a comparison purpose. As a result, carbon is approximately 51 %, 5 fluorine is approximately 46 %, and argon is approximately 3 %. The irradiation conditions of the Ar ion for the comparison are set such that the accelerating voltage is 500 V, the ion current is 100 nA, the irradiating time is 60 sec, and the scanning range on the surface of the sample is 5 mm × 5 mm.

10 [0032] In this case, the oxygen and the sodium constituting the contamination elements on the surface of the sample 4 are removed by the etching by the Ar ion, however, the ratio of carbon to fluorine is far from the original ratio (approximately 33 % and approximately 67 %, respectively), and 15 the quantitative results show that carbon is present more than fluorine. In other words, the quantitative value is far from the composition of the inner portion of the sample 4. Furthermore, as a result of observing the surface of the sample 4 by the electron microscope in the case of irradiating 20 the Ar ion, a damage which is not negligible is recognized on the surface of the sample 4.

[0033] As mentioned above, in accordance with the present embodiment, since the surface of the sample 4 can be uniformly etched to the level at which the damage on the surface of the 25 sample 4 is negligible, by irradiating the C₆₀ ion beam to the surface of the sample 4 before irradiating the characteristic X-ray to the surface of the sample 4, thereby enabling

removing a contaminant and an oxide film on the surface of the sample 4, it is possible to execute precise qualitative and quantitative analyses of the sample 4.

[0034] Furthermore, since the ion gun 8 irradiating the C₆₀ ion beam is not large, as compared with a unit forming a cluster (an ion source), a large-scale equipment is not required, and a cost increase can be restricted.

<Embodiment 2>

In the present embodiment, the X-ray photoelectron spectroscopy analysis of the polytetrafluoroethylene (PTFE) ((CF₂)_n) as the sample 4 is executed by using the electron spectroscopy analytical apparatus 1 in accordance with the embodiment 1 shown in Fig. 1. The structure of the electron spectroscopy analytical apparatus 1 is approximately the same as in the embodiment 1, and an overlapping description will not be repeated here.

[0035] A description will be given of an electron spectroscopy analysis method by an electron spectroscopy analytical apparatus 1 in accordance with an embodiment 2 of the present invention.

[0036] First, the sample 4 is mounted on the sample stage 5 within the vacuum chamber 2 through the open gate valve 9 by driving the carrier arm 3a of the carrier device 3 in the same manner as in the embodiment 1. Thereafter, the inner side of the vacuum chamber 2 is evacuated by a connected vacuum pump system (not shown) so as to be regulated to a predetermined pressure (a predetermined degree of vacuum), by closing the

gate valve 9. In the present embodiment, the pressure within the vacuum chamber 2 is set to 5×10^{-7} Pa.

[0037] Furthermore, the ion gun 8 is actuated and the C60 ion beam is irradiated to the surface of the sample 5 (polytetrafluoroethylene (PTFE) ((CF₂)_n)) 4. On the basis of the collision of the C60 ion beam with the surface of the sample 4, a contaminant, such as water, oil, fat, an inorganic material or the like and an oxide film attached to the surface of the sample 4 are etched so as to be removed. The 10 irradiation conditions of the C60 ion beam in the present embodiment at this time are set such that the accelerating voltage is 200 V to 30 kV, the ion current is 10 nA, the irradiating time is 60 sec, and the scanning range on the surface of the sample 4 is 5 mm × 5 mm.

15 [0038] Thereafter, a composition, a chemical state change and the like on the surface or in the depth direction of the sample 4 are analyzed (by an X-ray photoelectron spectroscopy analysis) by the electron energy analyzer 7, on the basis of the electrons emitted from the sample 4 by actuating the high-energy particle irradiating unit (the dual characteristic X-ray source) 6 and irradiating the characteristic X-ray to the surface of the sample 4. The irradiated characteristic X-ray in the present embodiment at this time has an energy of 8.048 keV, and copper is employed as a target of the characteristic 20 X-ray.

25 [0039] Fig. 2 shows the results of an X-ray photoelectron spectroscopy analysis (XPS spectrum) of carbon 1s line after

irradiating the C₆₀ ion beams having accelerating voltages of 10 kV (a in Fig. 2), 2 kV (b in Fig. 2) and 200 V (c in Fig. 2), respectively, to the surface of the sample 4, and etching the surface of the sample 4. The irradiating conditions of the 5 C₆₀ ion beam at this time are set such that the ion current is 10 nA and the irradiating time is 60 sec.

[0040] Additionally, d in Fig. 2 shows the results of an X-ray photoelectron spectroscopy analysis (XPS spectrum) of carbon 1s line after irradiating an Ar ion having an 10 accelerating voltage of 500 V to the surface of the sample 4, and etching the surface of the sample 4. The irradiating conditions of the Ar ion at this time are set such that the ion current is 100 nA and the irradiating time is 60 sec.

[0041] As shown in Fig. 2, in the case of the present 15 embodiment in which the C₆₀ ion beam is irradiated at the accelerating voltage of 2 kV (b in Fig. 2), the position of the XPS spectrum of the carbon 1s line becomes 293 eV (electron volt) showing a CF bond, and approximately coincides with a publication (Briggs and Beamson, *Handbook of X-ray 20 Photoelectron Spectroscopy of Polymer*, Wiley, 1991). In this case, in the case wherein the C₆₀ beam is irradiated at an accelerating voltage of 3 kV, approximately the same results can be obtained.

[0042] On the other hand, in the case wherein the C₆₀ ion 25 beam is irradiated at the accelerating voltage of 10 kV (a in Fig. 2), a little change in properties of the sample is recognized (practically having no problem). In the case

wherein the C₆₀ ion beam is irradiated at the accelerating voltage of 200 V (c in Fig. 2), the etching process on the surface of the sample is hardly executed, and a peak is recognized in the XPS spectrum on the basis of the 5 contamination on the surface of the sample. In the case wherein the C₆₀ ion beam is irradiated at an accelerating voltage of 300 V, the etching process on the surface of the sample is executed, and the change in properties of the sample is hardly recognized. Furthermore, in the case wherein the Ar 10 ion is irradiated at an accelerating voltage of 500 V (d in Fig. 2), the shape of the peak of the XPS spectrum is different, and the change in properties of the sample is recognized. Furthermore, in the case wherein the C₆₀ ion beam is irradiated at an accelerating voltage of 30 kV, the degree 15 of the change in properties of the sample practically has no problem.

[0043] As is apparent from the above-mentioned results, in order to securely acquire an X-ray photoelectron spectroscopy spectrum, the accelerating voltage of the irradiated C₆₀ ion beam is preferably 30 kV or less, and more preferably 10 kV or less and 300 V or more.

[0044] Furthermore, in each of the embodiments mentioned above, the characteristic X-ray source irradiating the characteristic X-ray is used as the high-energy particle 25 irradiating unit 6, however, it is possible to use an ultraviolet ray photoelectron spectroscopy analytical apparatus irradiating an ultraviolet ray, an Auger electron

spectroscopy analytical apparatus irradiating an electron, a positron exciting Auger electron spectroscopy analytical apparatus irradiating a positron, or the like in addition thereto.

5 [0045] Furthermore, each of the embodiments mentioned above is structured such that the sample 4 is carried within the vacuum chamber 2 after evacuating the inner side of the vacuum chamber 2 by the vacuum pump system (not shown) so as to be regulated to the predetermined pressure (degree of vacuum), however, the structure may be made such that after 10 mounting the sample 4 within the vacuum chamber 2, the inner side of the vacuum chamber 2 is evacuated by the vacuum pump system (not shown) so as to be regulated to the predetermined pressure (degree of vacuum).

15 [0046] Furthermore, each of the embodiments mentioned above is structured such that the C₆₀ ion beam is irradiated from the ion gun 8, however, the structure may be made such that a fullerene, for example, C₇₀ and C₈₄, an endohedral metalfullerene or the like is ionized so as to be irradiated, 20 in addition thereto.

Brief Description of Drawings

[0047] Fig. 1 is a skeleton schematic view showing an electron spectroscopy analytical apparatus in accordance with embodiments 1 and 2 of the present invention; and

25 Fig. 2 is a view showing results of an X-ray photoelectron spectroscopy analysis of carbon 1s line after irradiating a C₆₀ ion beam to a surface of a sample by

changing an accelerating voltage.

Description of Reference Numerals

[0048] 1 Electron spectroscopy analytical apparatus

2 Vacuum chamber

5 3 Carrier device

4 Sample (sample to be analyzed)

6 High-energy particle irradiating unit

7 Electron energy analyzer (analyzer)

8 Ion gun